Static Freezing Transition at a Finite Temperature in a Quasi-One-Dimensional Deuteron Glass

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The dipolar freezing process of a quasi-one-dimensional betaine deuteron glass was studied using linear and nonlinear dielectric spectroscopy. The linear response as measured for frequencies 5 mHz $<$ ν $<$ 200 MHz was analyzed using the recently invented δ plot, providing evidence for a static freezing transition near 30 K. Measurements of the ergodic to nonergodic transition as well as of the incipient divergence of the nonlinear susceptibility yield independent confirmation of this quasistatic freezing transition temperature. The critical exponent describing the nonlinear behavior is found to be $\gamma = 1$, compatible with mean-field predictions.

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In glass-forming matter it is still an open question whether there exists a static freezing transition into the glassy state at a finite temperature. This is not only true for the case of supercooled liquids [1] but also for model systems like spin glasses [2] and orientational glasses [3] (OG). In the latter cases one can take advantage of the fact that an order parameter can be defined theoretically [4] and determined experimentally using various techniques [5]. The linear response of, and the relaxation dynamics in, OG do not usually show an unambiguous signature of the transition from the ergodic to the nonergodic state. At this transition also the order parameter is typically smeared out because of random field effects, and therefore models are required in order to allow statements about static freezing temperatures T_f [4,6]. For a model independent determination of T_f more sophisticated experimental approaches are required. As suggested by the theory of spin glasses [2], these include measurements of the response of the orientational degrees of freedom not only to small but also to large external fields [7–9].

In this Letter we report on linear and nonlinear dielectric susceptibility measurements carried out on the betaine deuteron glass D-BP:BPI (40:60) which is a solid solution of the antiferroelectric betaine phosphate (BP) and the ferroelectric betaine phosphite (BPI) [3]. Protonated betaine proton glasses have been studied previously, mostly using dielectric permittivity measurements [10,11]. Analogous to the situation in KDP-type OG [12], at intermediate concentrations the frustrated interactions between the protons (or deuterons) located in hydrogen bonds connecting the phosphate or phosphoric tetrahedra lead to a dipolar glass state devoid of long range orientational order. What makes the betaine systems particularly interesting is the fact that here the hydrogen bonds form linear chains along the monoclinic b axis while in the KDP-type OG a three-dimensional hydrogen network exists, and it is noted that the reduced effective dimensionality of the dipolar coupling has stimulated considerable theoretical efforts [13,14].

Betaine single crystals of optical quality were grown by slow evaporation from deuterated aqueous solutions. The BP:BPI ratio of 40:60 refers to the nominal composition. For the dielectric measurements, single crystals were cut perpendicular to the monoclinic b axis to dimensions of typically $10 \times 10 \times 1$ mm^3. The large faces of the crystal slabs were covered with Cr/Au electrodes. The uncertainty in the geometrical capacitances is estimated to be 10%. For the dielectric measurements below 1 kHz a modified Sawyer-Tower circuit was used which allowed not only to apply small ac signals but, additionally, also large dc fields, thus enabling the measurement of the nonlinear susceptibility χ_{NL} [15]. For measurements of the complex dielectric constant $\varepsilon = 1 + \chi = \varepsilon' - i\varepsilon''$ in the frequency range 20 Hz $<$ ν $<$ 200 MHz, commercial equipment was used (models 4284A and 4192A from Hewlett-Packard).

In Fig. 1 we show the real and imaginary parts of the dielectric constant as measured in a wide frequency range for a number of temperatures. The smeared steps in ε' and the broad loss peaks in ε'' signal the slowing down of the dipolar degrees of freedom, i.e., the hopping motion of the acid deuterons in the double well potentials set up by the hydrogen bonds, on the time scale of the experiments. It is clear that the characteristic relaxation rates ν_p read off from the maximum of the loss peaks show an enormous variation with temperature and that the loss peaks broaden dramatically upon cooling.

The solid lines in Fig. 1 have been calculated using the phenomenological Havriliak-Negami equation which incorporates a width parameter α and an asymmetry parameter β [16]. Using this ansatz, a single relaxation time process is described by $\alpha = 1$ and $\beta = 1$. With decreasing temperature the width parameter decreases linearly, with $\alpha = 0.0112T$ indicating a diverging width for $T \rightarrow 0$. The asymmetry parameter β is 0.5 ± 0.1

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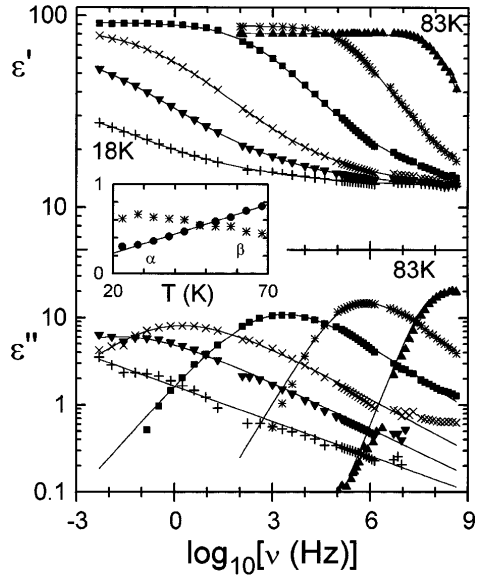

FIG. 1. Frequency dependence of ε' (upper frame) and ε'' (lower frame) of the complex dielectric constant of D-BP:BPI (40:60) as measured for frequencies 5 mHz $< \nu <$ 200 MHz and for the following temperatures: 18, 23, 28, 38, 53, and 83 K. Note that ε'' is given in a double logarithmic representation. The lines are calculated using the Havriliak-Negami equation with a width parameter α and asymmetry parameter β as given in the inset.

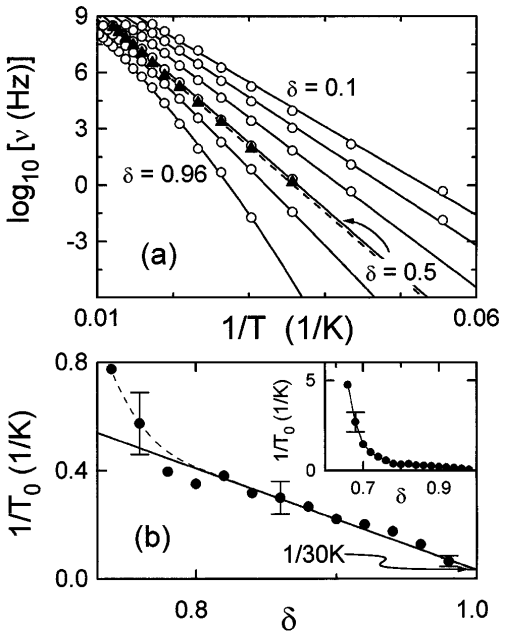

FIG. 2. (a) Arrhenius representation (δ plot) of data obtained from the reduced dielectric constant $\delta(\nu) = [\varepsilon'(\nu) - \varepsilon_\infty]/[\varepsilon_s - \varepsilon_\infty]$ in D-BP:BPI (40:60) according to the procedure suggested by Kutnjak *et al.* [17] (open circles) and from the loss peak frequencies (solid triangles). The solid lines are fits using the Vogel-Fulcher expression given in the text. (b) Inverse Vogel temperatures $1/T_0$ as obtained for $\delta > 0.7$. The solid line suggests a Vogel temperature of about 30 K for $\delta \to 1$. The inset shows the incipient divergence of $1/T_0$ for decreasing δ. Lines in the lower panel are drawn to guide the eyes.

and exhibits a minor temperature variation only. We have shown recently for the case of protonated betaine mixed crystals that random fields produced by substitutional disorder are responsible for the increase in the width of the relaxation peaks [11]. This effect could be described by a temperature independent Gaussian distribution of energy barriers. This symmetric broadening has to be convoluted with the asymmetry of the primary response which in structural glass formers is characterized by the time derivative of the Laplace transform of a Kohlrausch function [11].

Without going into further details here we would like to draw attention to the fact that for protonated BP:BPI crystals the loss peak frequency ν_p exhibited purely thermally activated behavior for all compositions [10,11]. This is in contrast to the findings in KDP-type proton glasses [8,12] and at first glance could be taken as indicating a less cooperative freezing dynamics due to the reduced dimensionality in the mixed betaines.

The peak maxima of the dielectric loss in D-BP:BPI (40:60) are shown in Fig. 2(a) as solid triangles and are seen to also obey an Arrhenius law $\nu_p = \nu_0 \exp(-E/k_B T)$ with an attempt frequency $\nu_0 = 5$ THz and an activation barrier of $E/k_B = 809$ K. Recently, Kutnjak *et al.* [17] have suggested obtaining more detailed information about the distribution of relaxation times by analyzing not the imaginary but rather the real part of the dielectric permittivity in a clever way. To this end they introduced a variable $\delta(\nu) = [\varepsilon'(\nu) - \varepsilon_\infty]/[\varepsilon_s - \varepsilon_\infty]$ with ε_s and ε_∞ denoting static and high-frequency permittivity, respectively. By determining the value of the frequency ν_δ for a given δ and for all accessible temperatures, one can then construct an Arrhenius plot, the so-called δ plot shown for D-BP:BPI (40:60) in Fig. 2(a) [18]. It is seen that the smearing of the steps in ε' or the associated loss peak width as determined from the difference between the lines with $\delta = 0.28$ and 0.74, say, increases roughly as $1/T$. This is characteristic for the existence of a distribution of energy barriers. For $\delta = 0.5$ the characteristic frequencies ν_δ are almost identical to ν_p, as can be expected for a nearly symmetrical distribution of relaxation times (cf. Fig. 1). Other notable cases are $\delta \to 0$ and $\delta \to 1$ which correspond to the high- and low-frequency ends of the spectrum of relaxation times, respectively. Most interesting is of course the limit $\delta = 1$ which reveals the temperature evolution of the slowest element in the spectrum.

From Fig. 2(a) it is evident that for $\delta > 0.7$ the curves develop considerable curvature. The solid lines in this figure have been calculated using the Vogel-Fulcher expression $\nu_\delta = \nu_0 \exp[-B/(T - T_0)]$ with a δ-dependent Vogel temperature T_0. Its value in the limit $\delta = 1$ corresponds to the static freezing temperature [17]. In Fig. 2(b) we show $1/T_0$ as a function of δ for $0.6 < \delta <$

0.96: $1/T_0$ is an almost linear function of δ for large values ($\delta > 0.75$) and tends to diverge for decreasing δ [see inset of Fig. 2(b)]. It is clearly seen that for $\delta \rightarrow 1$ the Vogel temperature extrapolates to about 30 K. It has to be noted, however, that no theoretical predictions are available on how this extrapolation should be carried out, and hence it can be stated with certainty from the data presented in Fig. 2 only that T_f is higher than 20 K.

In order to determine the freezing temperature more precisely we have carried out temperature cycles under bias-field and zero-field conditions. This procedure can yield valuable information on the nature of the OG state, since one typical signature of the nonergodic regime is that material properties depend on the conditions under which they were entered [8,9]. In our study we have used relatively small fields in order to obtain the near equilibrium freezing temperature, since it is known that T_f depends slightly on the externally applied field [19]. We have also employed relatively low temperature ramping rates of about 1–2 K/min and find no significant rate dependence, although for larger rate variations such a dependence may become observable [20]. Figure 3 shows the polarization as measured under field heating (FH), field cooling (FC), and zero-field heating (ZFH) conditions subsequent to an initial zero-field cooldown (ZFC). It is clearly seen that the FH and FC runs yield compatible results for $T > 30$ K only, but below this temperature significantly smaller polarizations are obtained by FH, indicating a breakdown of ergodicity. Upon the final ZFH the remnant polarization is seen to vanish for $T > 30$ K, confirming the restoration of ergodicity at this temperature, thus confirming the result obtained above by analyzing the dynamical response.

It was recognized a long time ago that in spin glasses the nonlinear susceptibility χ_{SG} plays the same role as the linear susceptibility in ferromagnets, i.e., it should diverge at T_f (Ref. [2]). χ_{SG} is directly related to the nonlinear susceptibility $\chi_{NL} = (\chi_{SG} - 2/3)/T^3$ obtained by measuring the ac response of the material in the presence of strong dc field. We have measured χ_{NL} at a frequency of 90 Hz with a bias field of 1 kV/mm. As shown in Fig. 4, this quantity shows a temperature dependence which is much more pronounced than that of the linear susceptibility measured at the same frequency. We have analyzed the temperature dependence of χ_{NL} in the temperature range where no dispersion occurs (see Fig. 4) in order to maintain quasistatic conditions. The data can be well described using the scaling ansatz $\chi_{NL} = \chi_1^4/(T - T_f)^\gamma$. Using the mean field prediction for the exponent $\gamma = 1$ we find that $T_f = 28$ K, i.e., χ_{NL} diverges on approaching the Almeida-Thouless line [21]. Or, likewise, by fixing T_f to 30 K, the value yielded by the other experiments described in this Letter, we obtain $\gamma = 1.04 \pm 0.10$. This exponent meets the theoretical predictions of a random bond–random field model developed for orientational glasses [21]. Experimentally, a value of 1.7 has been determined for the dipolar glass $KTaO_3$:Na [7], while γ's ranging from 0.95 to 1.7 have been observed in the quadrupolar glass KBr:KCN [9]. It may well be that in these experiments the exponents are affected by the appearance of (unnoticed) relaxation processes in the higher order susceptibilities which has been carefully avoided in the present investigation. We point out the fact that while the freezing transition in the betaine dipolar glass seems to be describable using mean-field theory, this is in contrast to the situation in at least one other dipole glass [22].

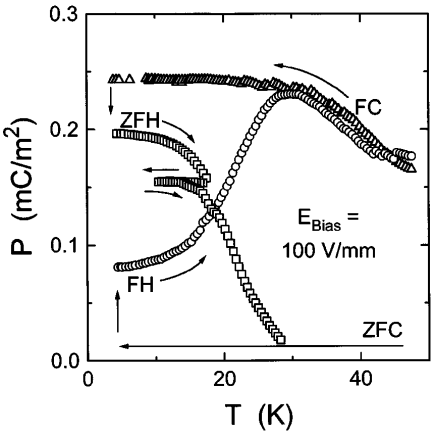

FIG. 3. Polarization in D-BP:BPI (40:60) as measured under zero-field and nonzero-field conditions while ramping the temperature at a constant rate of 1 K/min in the sequence ZFC-FH-FC-ZFH as indicated by the arrows. The ergodic to nonergodic transition takes place at the point where FH and FC polarizations split, i.e., at 30 K. Also, at the same temperature, the remnant polarization thaws upon heating.

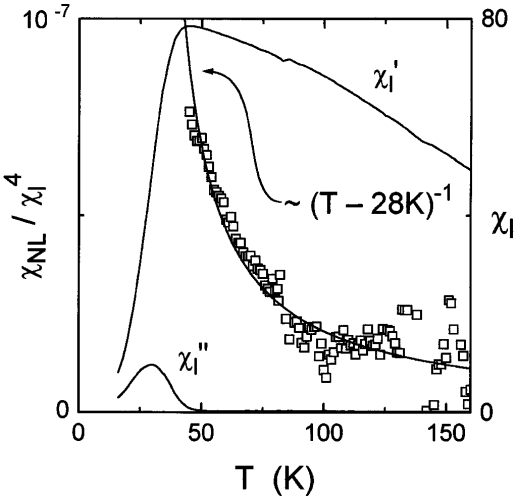

FIG. 4.. Temperature dependence of the nonlinear susceptibility in D-BP:BPI (40:60) plotted as χ_{NL}/χ_1^4. The local susceptibility χ_{NL} was measured in a bias field of 1 kV/mm, using a small amplitude ac signal of 90 Hz. For comparison, real and imaginary parts of the linear susceptibility $\varepsilon = \varepsilon_\infty + \chi_1$ are also shown. The solid line is calculated using $\chi_{NL}/\chi_1^4 = (T - T_f)^{-\gamma}$ with $\gamma = 1$ and $T_f = 28$ K.

Finally, we note that we have started to measure the second harmonic susceptibility χ_2 generated by the application of a large external ac field. Surprisingly, we find $\chi_2 \neq 0$ (not shown), indicating the presence of inversion symmetry breaking local fields. Such effects have recently been predicted by Monte Carlo simulations to occur in 3-state Potts models with nearest neighbor interactions [23]. Further theoretical studies of this question are warranted since it is not clear how the case of the quasi-one-dimensional deuteron glass can be mapped onto the 3-state Potts model. Our experimental results for χ_2 are again compatible with an extrapolated divergence of χ_2 at about 30 K, but due to the relative smallness of this quantity, the quality of the data is not sufficient to permit more quantitative statements at present.

Taken together, the evidence presented here suggests that in D-BP:BPI (40:60) the static freezing transition can be viewed as a dynamic phase transition. Corresponding theoretical scenarios have been worked out in detail by Bengtzelius, Götze, and Sjölander [24] and have been adapted by Bostoen and Michel for quadrupolar glasses, such as KBr:KCN [25]. It would be highly desirable to develop similar concepts also for the case of (effectively low-dimensional) dipolar glasses.

To summarize, we have carried out measurements on a quasi-one-dimensional dipole glass in small and large external electrical fields. The techniques used include broad-band dielectric spectroscopy and quasistatic polarization experiments, as well as the investigation of the nonlinear electrical susceptibility. These three independent experimental approaches when evaluated in the quasistatic limit yield a unique freezing temperature of $T_f = 30 \pm 2$ K in D-BP:BPI (40:60). Furthermore, the measurement of χ_{NL} provides evidence for the applicability of mean-field theory to the freezing process in a quasi-one-dimensional dipole glass.

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